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## Optical and structural properties of BeCdSe/ZnSe QW heterostructures grown by MBE

S. V. Ivanov<sup>†,‡</sup>, O. V. Nekrutkina<sup>†</sup>, V. A. Kaygorodov<sup>†,§</sup>, T. V. Shubina<sup>†</sup>,  
P. S. Kop'ev<sup>†</sup>, G. Reuscher<sup>‡</sup>, V. Wagner<sup>‡</sup>, J. Geurts<sup>‡</sup>, A. Waag<sup>‡</sup>  
and G. Landwehr<sup>‡</sup>

<sup>†</sup> Ioffe Physico-Technical Institute, St Petersburg, Russia

<sup>‡</sup> Physikalisches Institut der Universität Würzburg, Am Hubland,

D-97074 Würzburg, Germany

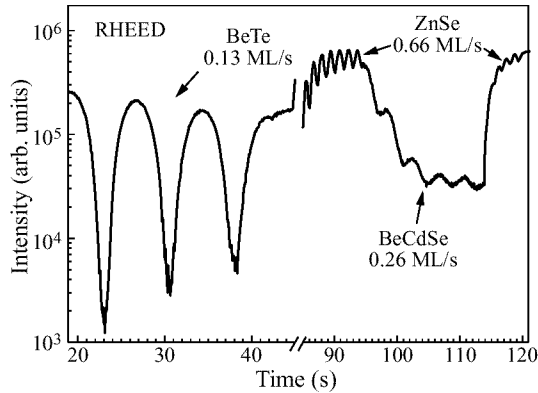
<sup>§</sup> St Petersburg Electrotechnical University, St Petersburg 197376, Russia

II–VI wide-gap heterostructures still remain the most natural candidates for blue-green laser diode (LD) applications, although demonstrating so far a non-sufficient device lifetime (less than 500 hours [1]), because this spectral range (<450 nm) is hardly reachable by III-nitrides based lasers. It is generally believed now that the large stress accumulated in a lattice-mismatched quantum well (QW) active region (like ZnCdSe one) causes enhanced multiplication and diffusion of extended and point defects. This effect in combination with a low threshold of defect formation, characteristic of ZnSe-based compounds, seems to be responsible for a so called “slow” LD degradation. Thus, the need in low-stress high-stiffness QW structures for the active region of blue-green II–VI lasers and light-emitting diodes stimulates a search of new suitable materials.

Recently a new material for the laser active region — BeCdSe — has been proposed [2]. Despite expectations of a very wide instability region for this alloy, it has been predicted that stable  $\text{Be}_x\text{Cd}_{1-x}\text{Se}$  alloys with composition lattice-matched to GaAs ( $x \sim 0.46$ ) can be grown by molecular beam epitaxy (MBE) until a relaxation of elastic stress in the layer occurs. The high Be content in this alloy is believed to make the crystalline lattice much harder than in commonly used ZnCdSSe alloys. Since previous study was mainly focused on  $x = 0.0$ – $0.33$  range, only rough extrapolation of an energy gap ( $E_g$ ) versus  $x$  dependence to the lattice-matched composition region has been made, taking optical bowing parameter equal to 3 eV. It gave nearly equal  $E_g$  values for ZnSe and  $\text{Be}_{0.47}\text{Cd}_{0.53}\text{Se}$  alloy, leaving questionable the possibility to obtain the lattice-matched BeCdSe/ZnSe QW suitable for laser applications.

In this paper we study optical and structural properties of the  $\text{Be}_x\text{Cd}_{1-x}\text{Se}/\text{ZnSe}$  QWs grown by MBE in the composition range close to the compound lattice-matched to GaAs. Bright low-temperature (80 K) photoluminescence (PL) in the 2.45–2.66 eV range, preserving up to 300 K, has been obtained for  $x = 0.36$ – $0.49$  estimated from reflection high energy electron diffraction (RHEED) and x-ray diffraction (XRD) measurements. Much stronger optical bowing in this alloy system has been found, as compared to previously estimated one.

Structures with both single QW (SQW) and multiple QWs (MQW) were grown either in a conventional MBE mode or by a sub-monolayer digital alloying (SDA) technique at a substrate temperature  $T_s = 300^\circ\text{C}$  on (001) GaAs substrates, using a solid source MBE setup (Riber 2300). Except for BeCdSe/ZnSe QWs of either 2 or  $\sim 10$  nm thick, separated by  $\sim 10$  nm ZnSe barriers, the structures involve 50–100 nm- $\text{Zn}_{0.97}\text{Be}_{0.03}\text{Se}$  claddings and a thin BeTe buffer layer grown at  $350^\circ\text{C}$ . Structural properties of the multi-layer samples

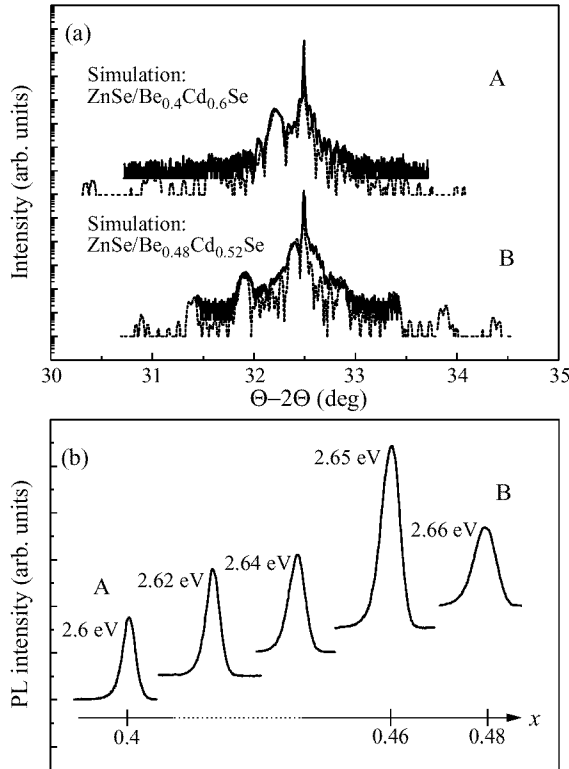


**Fig. 1.** RHEED oscillation measurements of growth rate and composition during MBE growth of a BeTe buffer and one period of a BeCdSe/ZnSe MQW structure.

were analysed by a dynamic simulation of (004) XRD  $\theta-2\theta$  rocking curves obtained using a Philips X'pert diffractometer equipped with a four-crystal Ge 220 monochromator. PL spectroscopy was performed using a 325 nm excitation line of a He-Cd laser. Growth rate and alloy composition were additionally controlled by RHEED oscillation technique, as shown in Fig. 1 where a ratio of the BeTe buffer to the BeCdSe QW growth rates (in monolayer/s) gives a rather accurate estimation of the alloy composition.

To study a modification in BeCdSe optical properties with Be content, two 2 nm-BeCdSe/9 nm-ZnSe MQW structures with significant grade of the Be content along a wafer surface were grown without rotation in MBE and SDA modes. As the XRD data analysis demonstrates the Be content variation across the MBE structure surface from  $x = 0.40$  to  $x = 0.48$  (Fig. 2(a)), with the maximal composition corresponding to the point of RHEED registration, PL peak gradually shifts to higher energies (Fig. 2(b)), still remaining at 160 meV below  $E_g$  of ZnSe. Another important feature of the PL spectra is an existence of a pronounced maximum in the peak intensity *versus* Be composition, relating to a pseudomorphic composition of  $x = 0.46-0.47$ , as estimated from XRD data. PL spectra of the SDA structure with the Be content changing from 0.36 to 0.49 demonstrate the same behavior, with the most intensive PL peak being placed at the same energy of 2.65 eV. Since strain-induced defects reduce a quantum efficiency of QW structures, one could expect an existence of the PL peak corresponding to a non-strained BeCdSe layer, which is appreciably more intensive than others related to the QWs with increasing lattice mismatch. One should mention that both MQW structures demonstrate very bright PL of nearly the same intensity, independently of the growth mode, although XRD analysis shows higher structural quality of SDA MQW structure even at minimum  $x = 0.36$ .

Despite the rather large lattice mismatch variation in the MQW structures, with the lowest  $x = 0.36$  being somewhere at the boundary of the BeCdSe instability region thermodynamically calculated in [2], no pronounced signature of phase separation has been observed probably due to the small QW thickness as compared to the critical one. It is confirmed additionally by two 2 nm SQW structures with  $x \sim 0.35$  and  $x \sim 0.4$ , whereas a decrease in  $x$  below 0.33 causes already a pronounced phase separation even in 2 nm QWs [2]. Contrary to that, a 10 nm-BeCdSe/10 nm-ZnSe MQW structure, also grown with the intentional Be composition gradient, has revealed a dramatic disturbance of structural properties due to the phase separation at relatively small deviation of  $x$  from the lattice-



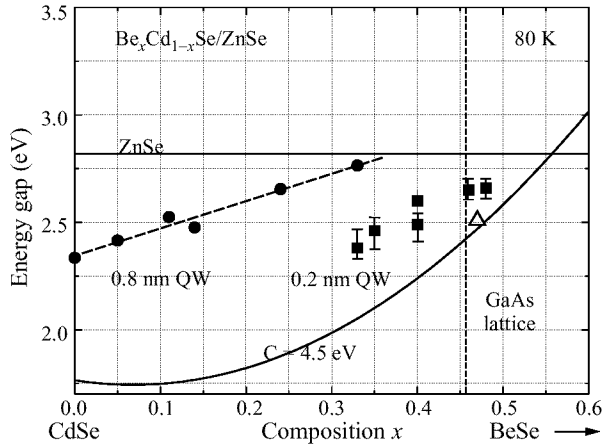
**Fig. 2.** (a) XRD  $\theta$ - $2\theta$ -rocking curves of BeCdSe/ZnSe MQW structure taken from two opposite points along the grade of Be content: experimental (solid curves) and theoretical simulations (dashed curves). (b) PL spectra (80 K) of the same structure taken along the grade of Be content. A and B denote points where XRD measurements were performed (see Fig. 2(a)).

matched composition, as observed *in situ* by RHEED and *ex situ* by XRD and PL and will be reported in details elsewhere. This effect is probably caused by exceeding the QW critical thickness, followed by elastic stress relaxation resulting in dramatic CdSe-BeSe phase diagram transformation [2].

Figure 3 presents an estimation of the BeCdSe  $E_g$  versus  $x$  behavior, which has been done using the PL data on all ZnSe/BeCdSe SQW and MQW structures discussed in this work (shown by squares and triangle). Additionally, PL data on 0.8 nm BeCdSe/ZnSe SQWs from [2] are given by circles. One should note that the point with  $x \sim 0.33$  can be regarded only as a very rough value due to an onset of the phase separation process. Solid curve is a result of theoretical estimation of the BeCdSe energy gap bowing in accordance with

$$E_g(\text{BeCdSe}) = (1 - x)E_g(\text{CdSe}) + xE_g(\text{BeSe}) - x(1 - x)C,$$

where  $C$  is the bowing parameter estimated as 4.5 eV in this case. This value is even higher than 3.0 eV found in [2], using an extrapolation of experimental slope obtained for the narrow 0.8 nm QWs with  $x$  at the CdSe-rich composition side. The new data allow us to consider the lattice-matched BeCdSe/ZnSe QWs as very promising structures for the active region of II-VI blue-green laser, which can provide sufficient electronic confinement. The question of band-offsets in the BeCdSe/ZnSe system still remains unclear, but



**Fig. 3.**  $E_g$  versus  $x$  dependence for  $\text{Be}_x\text{Cd}_{1-x}\text{Se}$  system. Experimental PL peak energies obtained in this work are shown for  $\text{Be}_x\text{Cd}_{1-x}\text{Se}/\text{ZnSe}$  QWs of 2 nm (squares) and 10 nm (triangle) in a thickness. Error bars include possible variation of the QW thickness. Solid curve is a theoretical estimation using bowing parameter  $C = 4.5$  eV. Circles are the experimental data presented in Ref. [2] for 0.8 nm QWs.

ZnSe/BeCdSe QW is expected to be of type-I due to the absence of blue shift of the PL peak with a  $\sim 150$  time increase in an excitation power.

In summary, SQW and MQW structures of different thicknesses (2–10 nm), based on a new II–VI compositional material  $\text{Be}_x\text{Cd}_{1-x}\text{Se}$  with a Be content ranging from 33% to 50% have been grown by MBE using different growth modes. The structures have demonstrated bright PL up to room temperature and no phase separation phenomena in the vicinity of  $x = 0.46$  corresponding to a composition lattice-matched to GaAs. Large energy gap bowing ( $C = 4.5$  eV), refined using new experimental PL data, permits one to consider BeCdSe alloys with large Be content as suitable materials for a QW active region of ZnSe-based blue-green laser diodes.

#### Acknowledgements

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